Future metal waste forms: Impact of cladding type and zirconium loading on microstructure and corrosion

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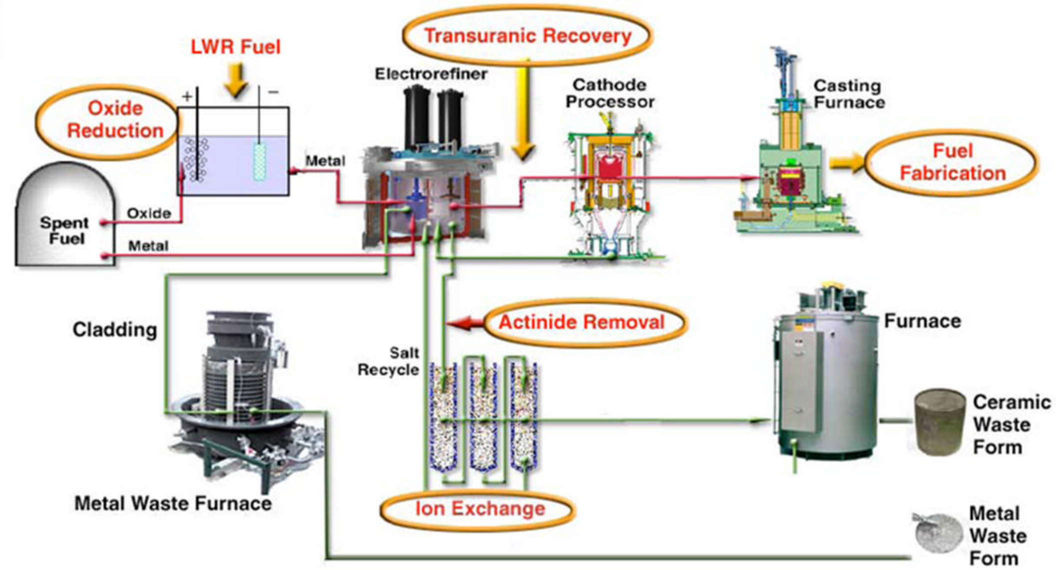
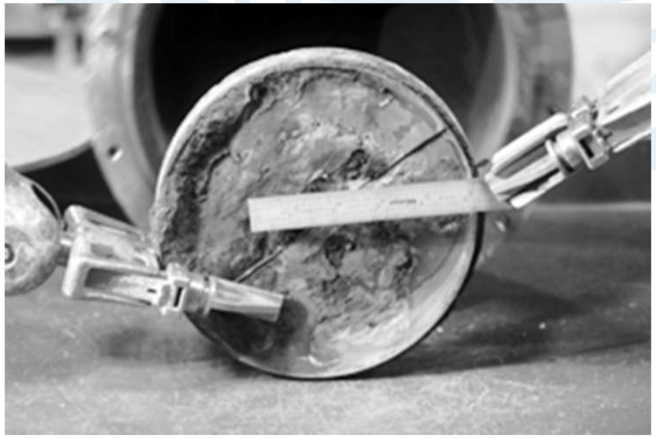
Waste Form Approach: EMT Process



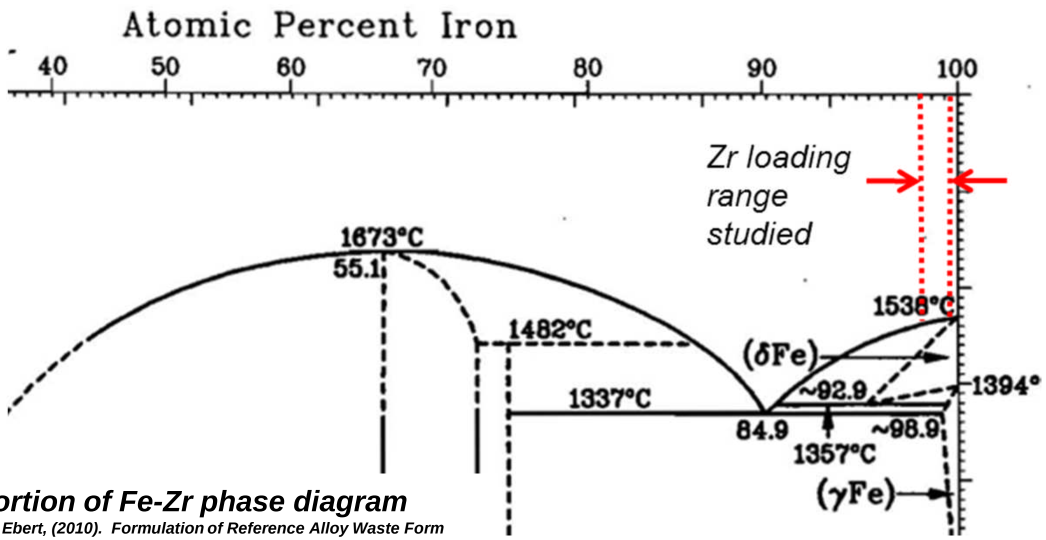


Metal waste form ingot made from irradiated EBR-II hulls *(D.D. Keiser Jr. et al. / Journal of Nuclear Materials 279 (2000) 234-244)*

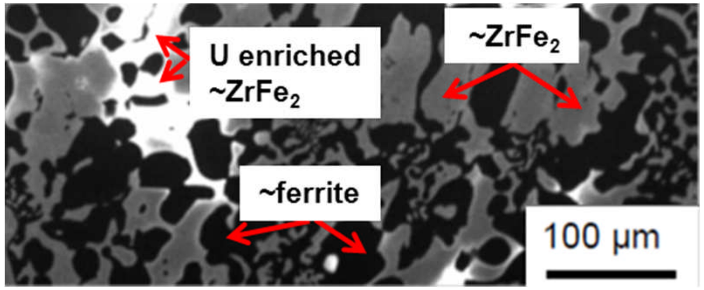
- **Objective: Find minimum Zr concentration needed to capture all U**
- **Past experience with EBR-II to influence future process flows**
  - For metal fuels: fuel or blanket fuel pins chopped and placed in 304 SS anode basket
  - Reactive elements dissolved electrochemically: Pu, U, most fission products, etc…
  - More inert fuel pin components remain in anode basket (UDS): 304 SS, D9, or HT9 cladding, Zr, platinoid group FP’s, other trace impurities from inefficiencies such as ~1 % U
  - Cladding with UDS melted in crucible with Zr trim to make a low melting eutectic and potentially some DU for proliferation resistance

Alloy Composition Effects: Zr

- 316L SS and HT9 used as Fe feedstocks (HT9 → virtually no Ni)
- Zr/U atomic ratios range from 3 to 1/3
- Mo content (SS: 2.6-3.0 at%, HT9: 1.6-1.9) is important because a Mo-Cr-Fe intermetallic phase may be formed in addition to, or instead of, the Zr-Ni-Fe intermetallic that has previously sequestered the U



Portion of Fe-Zr phase diagram
(W. Ebert, (2010). Formulation of Reference Alloy Waste Form RAW-1, Argonne National Laboratory Technical Document, FCRD-WAST- 2011-000004.)



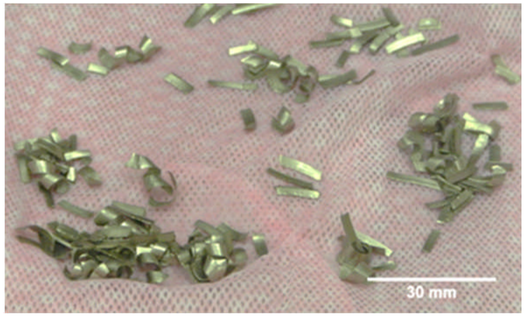
SS-15Zr-5U alloy *(D.D. Keiser Jr. et al. / Journal of Nuclear Materials 279 (2000) 234-244)*

Alloy Composition Effects: Zr

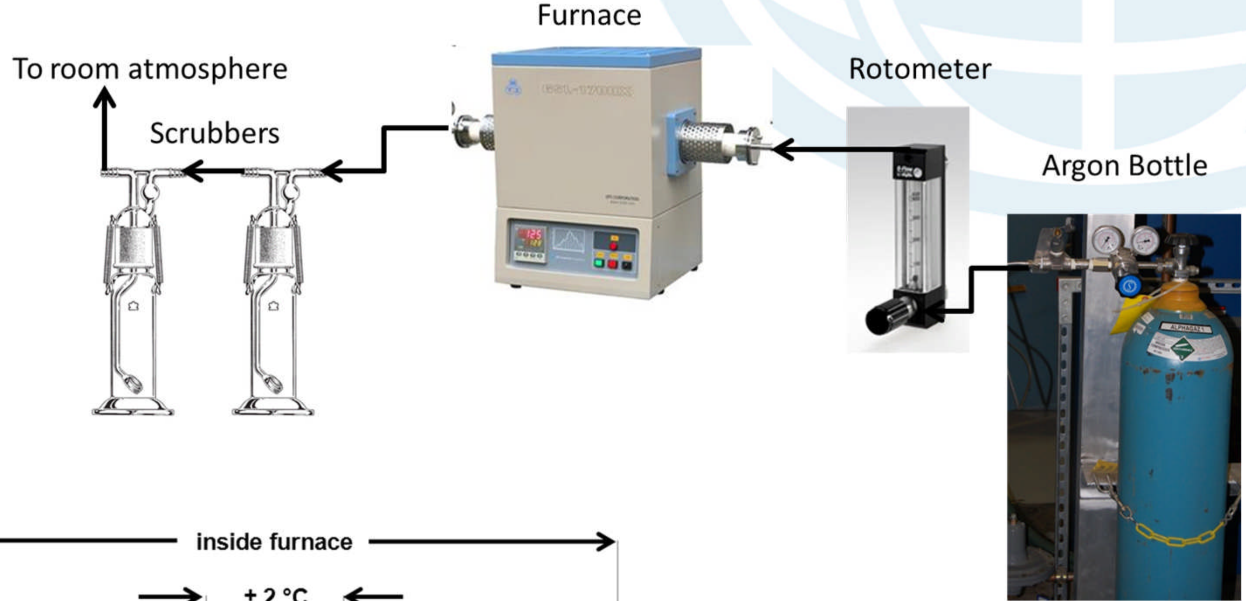
- **Post fabrication characterization**
  - Phase area contribution
  - Phase composition via EDS

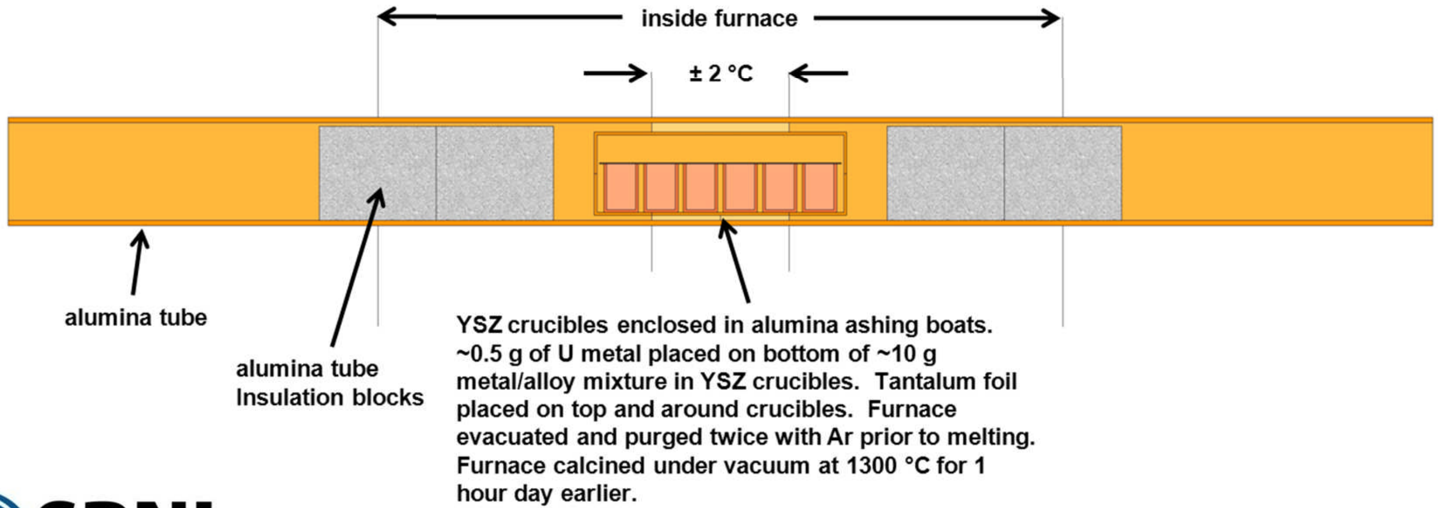
  May be used to aid determination of expected release rates for specific species
- **Electrochemical testing**
  - Does a hysteresis exist for any electrochemical parameters as a function of Zr content, and how would they affect corrosion and release rates?
  - Focus on collecting high quality electrochemical parameters of use for modeling
- **Initial assumptions based on EBR-II metal waste form experience**
  - Uranium segregates to ~$ZrFe_2$ phase
  - Less Zr will likely lead to higher melting point
  - Less Zr will likely lead to less $ZrFe_2$ phase
  - $MoFe_2$ phase may form
  - Ni often co-located with high U loadings, different U phase may be seen for HT9 cladding

Furnace Apparatus for Fabricating EMT Alloy Waste Forms



Cleaned and clipped U turnings





Electrometallurgical Processing Wastes: Compositions to be studied

- **EMT Zr/U test matrixes (all in atomic %)**

316SS Fe Base											
	Cr	**Mn**	**Fe**	**Ni**	**Mo**	**Zr**	**Ru**	**Pd**	**Re**	**Rh**	**U**
Zr/U ~ 2	17.9	1.5	58.4	10.7	2.5	2.3	1.1	1.1	1.1	1.1	1.2
Zr/U ~ 1	18.1	1.5	59.1	10.8	2.5	1.2	1.1	1.1	1.1	1.1	1.2
Zr/U ~ 1/3	18.3	1.5	59.5	10.9	2.5	0.4	1.1	1.1	1.1	1.1	1.2

	316SS	HT9
Cr	18.4	12.2
Fe	64.4	84.8
Ni	12.4	0.6

HT9 Fe Base											
	Cr	**Mn**	**Fe**	**Ni**	**Mo**	**Zr**	**Ru**	**Pd**	**Re**	**Rh**	**U**
Zr/U ~ 2	11.5	0.6	76.3	0.5	1.8	2.3	1.1	1.1	1.1	1.1	1.2
Zr/U ~ 1	11.7	0.7	77.1	0.5	1.8	1.2	1.1	1.1	1.1	1.1	1.2
Zr/U ~ 1/3	11.8	0.7	77.7	0.5	1.8	0.4	1.1	1.1	1.1	1.1	1.2

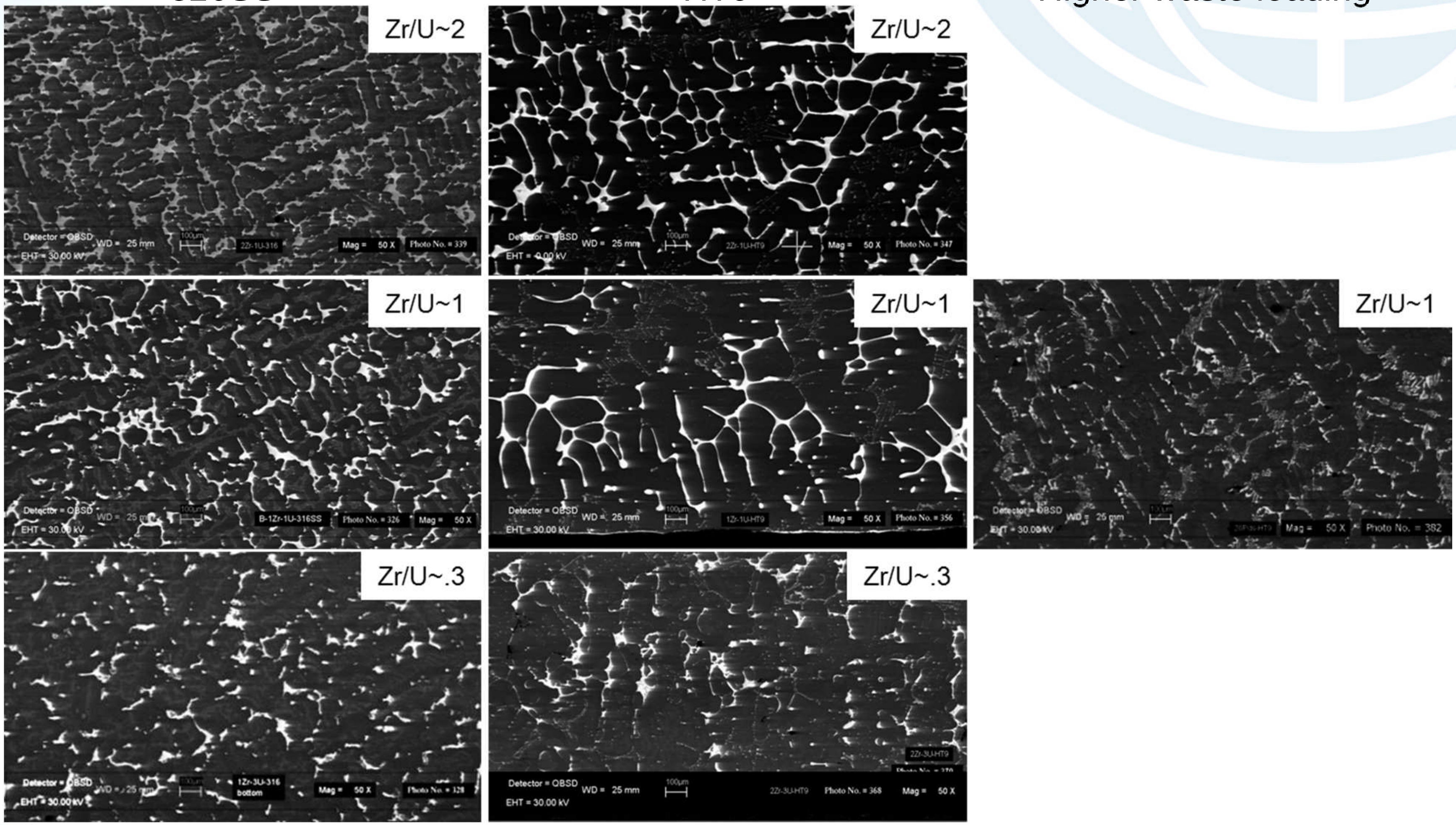
HT9 Fe Base (Zr/U ~ 1)											
	Cr	**Mn**	**Fe**	**Ni**	**Mo**	**Zr**	**Ru**	**Pd**	**Re**	**Rh**	**U**
~9 w% inert metals	11.7	0.7	77.1	0.5	1.8	1.2	1.1	1.1	1.1	1.1	1.2
~21 w% inert metals	10.0	0.6	66.3	0.4	6.8	1.0	5.3	4.3	1.5	1.5	1.0

Inert metals = Mo, Ru, Pd, Re, Rh

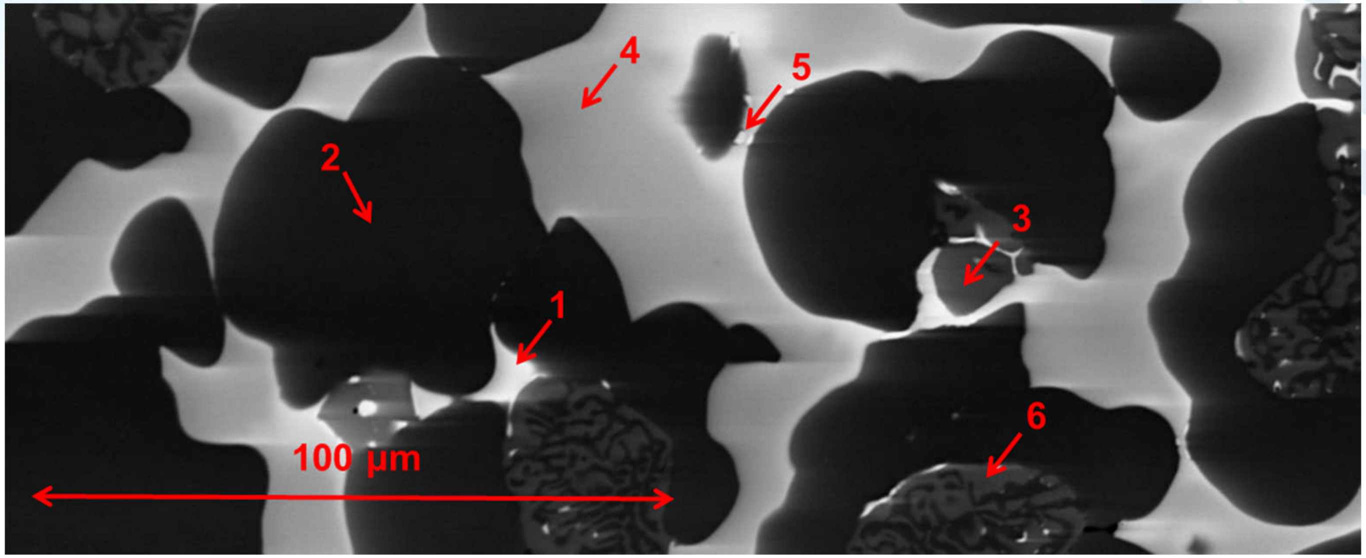
Inert metal loading for 316SS and HT9 alloys are all ~9 w% except for the one ~21 w% alloy

Low Mag Overview

316SS *HT9* *Higher waste loading*



316SS, Zr/U~2



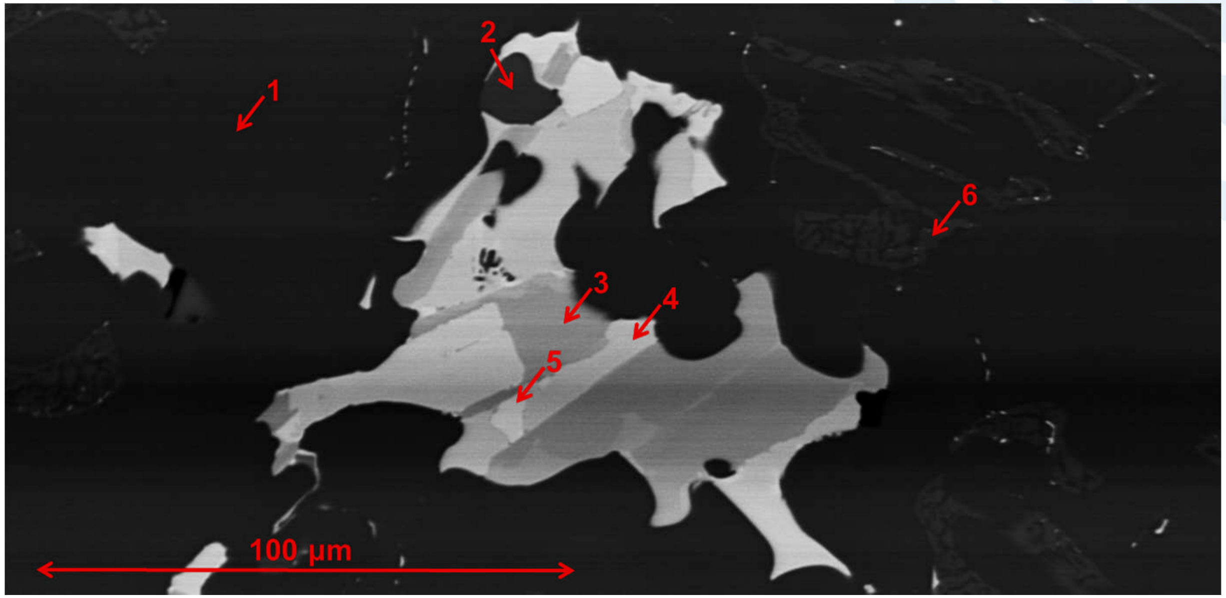
Note: Austenite and ferrite phases are distinct in BSE mode and sequester Re (Tc surrogate), and ferrite preferentially so. U appears to segregate exclusively to high Zr regions

Note: EDS results do not necessarily correspond to exact points in micrograph

	atomic %										
EDS Point	Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
1	4.9	1.8	33.8	29.0	8.1	0.4	0.0	3.8	4.0	0.0	14.2
2	17.8	3.5	63.0	10.3	0.0	2.3	1.0	0.5	0.5	1.0	0.0
3	26.9	3.9	52.1	4.7	0.0	7.7	1.6	0.4	0.2	2.4	0.1
4	3.4	1.8	33.6	27.4	22.5	1.9	0.0	1.2	4.7	0.0	3.5
5	2.7	1.4	27.0	25.6	12.4	1.2	0.0	1.0	16.8	0.0	11.9
6	27.0	4.0	52.3	4.6	0.0	7.4	1.6	0.3	0.4	2.3	0.1

316SS, Zr/U~1/3

Note: High Pd, U, and Ni composition regions with distinct boundaries detected in what would be primarily $ZrFe_2$ phase in higher Zr concentration waste forms

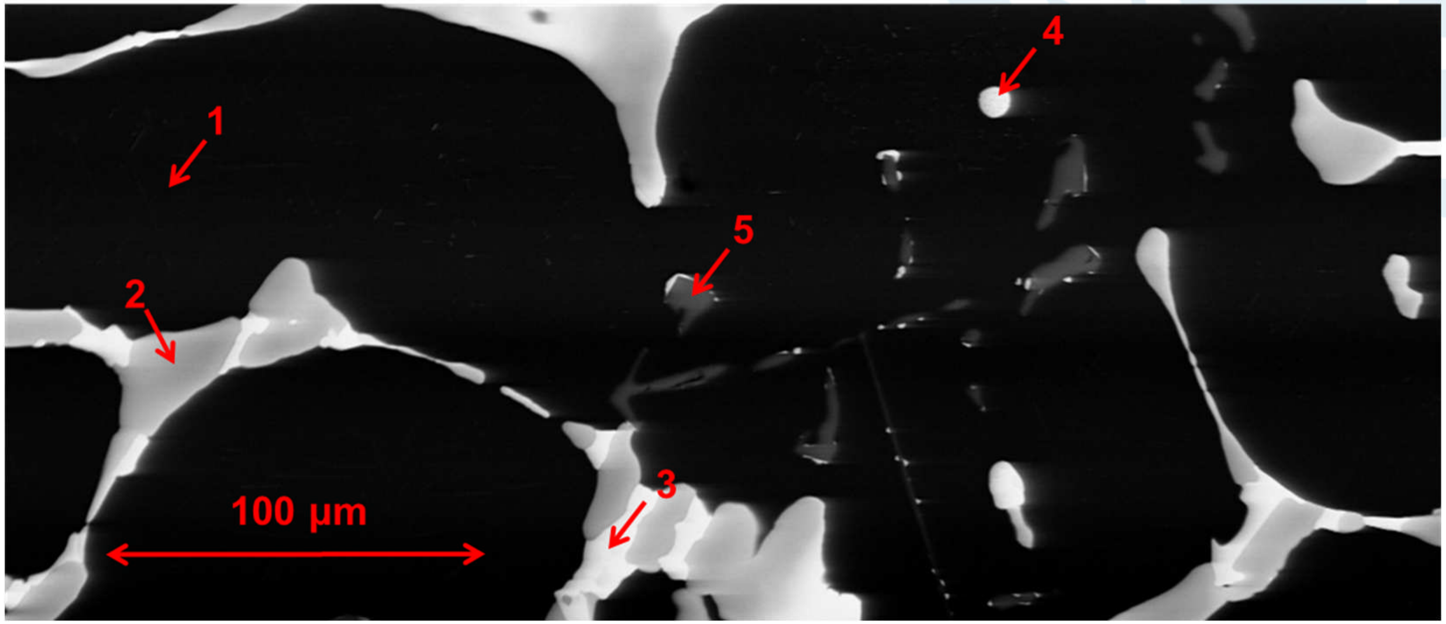


Note: EDS results do not necessarily correspond to exact points in micrograph

	Atomic %										
EDS Point	**Cr**	**Mn**	**Fe**	**Ni**	**Zr**	**Mo**	**Ru**	**Rh**	**Pd**	**Re**	**U**
1	18.2	3.4	60.6	11.0	0.0	2.9	1.0	0.7	0.9	1.3	0.1
2	26.5	3.8	49.6	5.2	0.0	9.4	2.0	0.5	0.3	2.7	0.1
3	2.0	1.0	25.6	37.2	12.2	0.6	0.0	3.0	6.6	0.0	11.8
5	0.0	0.0	3.5	24.6	6.0	0.0	0.0	13.6	31.1	0.0	21.3
4	2.0	2.1	30.4	29.9	6.8	0.0	1.6	4.5	4.3	0.0	18.4
6	23.4	3.4	55.5	6.5	0.0	6.3	1.5	0.5	0.4	2.6	0.1

HT9, Zr/U~2

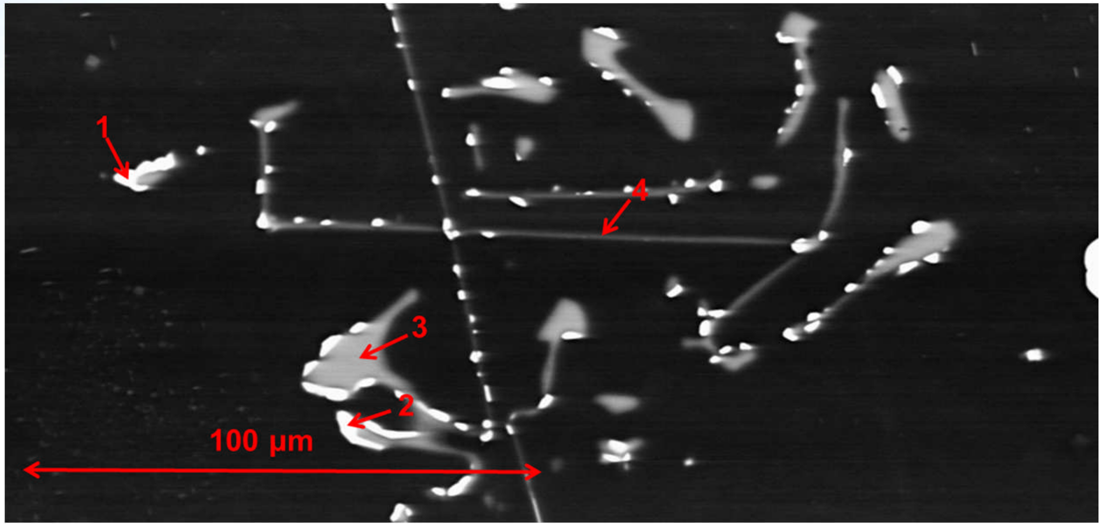
Note: only 1 $ZrFe_2$ and 1 $ZrPd_2$ compositional range detected (not so for other alloys in series). Nearly pure Zr regions detected. Needle like regions detected in all HT9 samples

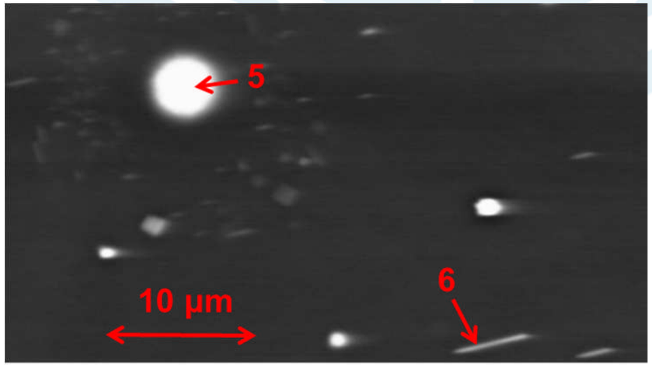


Note: EDS results do not necessarily correspond to exact points in micrograph

	atomic %										
EDS Point	Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
1	12.9	2.1	80.1	0.3	0.0	1.9	0.9	0.4	0.3	1.0	0.0
2	2.4	0.9	57.3	1.7	20.9	1.1	1.1	4.9	3.3	0.0	6.4
3	0.8	0.0	4.1	1.4	13.4	1.0	0.0	0.0	62.7	0.0	16.6
4	2.5	0.8	51.6	3.1	8.3	0.0	0.0	8.2	7.2	0.0	18.5
5	0.7	0.0	4.4	0.2	89.4	5.3	0.0	0.0	0.0	0.0	0.0

HT9, Zr/U~1



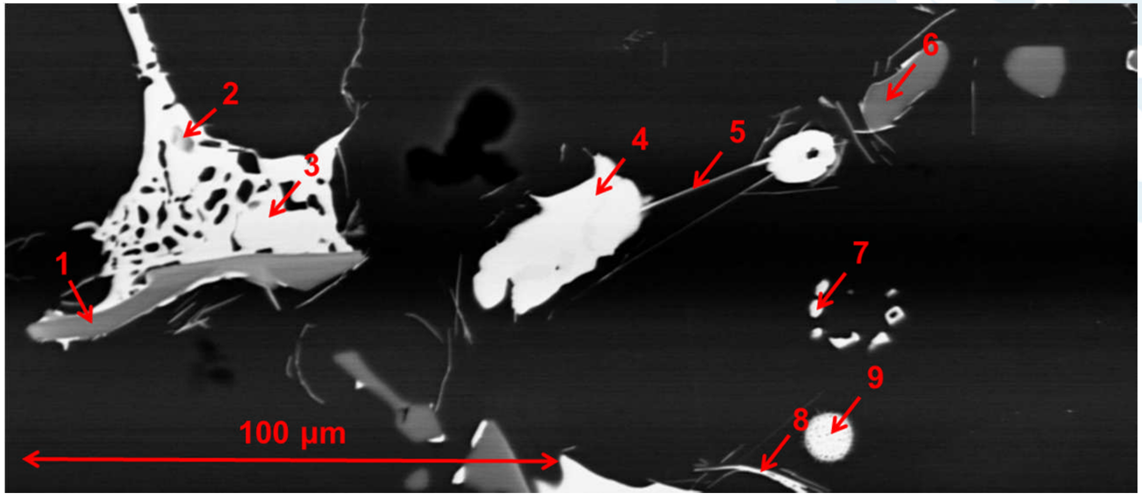


Note: EDS results do not necessarily correspond to exact points in micrograph

	Atomic %										
EDS Point	Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
1	2.0	0.2	11.5	0.8	41.2	2.9	0.0	0.0	32.3	0.0	9.1
2	1.5	0.0	9.6	1.2	21.1	1.7	0.0	0.0	51.2	0.0	13.8
3	0.4	0.0	2.4	0.0	91.8	5.3	0.0	0.0	0.0	0.0	0.1
4	11.7	1.9	72.8	0.4	9.5	2.2	0.9	0.5	0.2	0.0	0.0
5	1.9	0.6	39.2	3.8	10.2	0.0	0.0	12.7	11.7	0.0	19.8
6	12.6	2.0	78.4	0.4	0.4	2.0	0.0	0.0	2.3	1.0	1.0

HT9, Zr/U~1/3

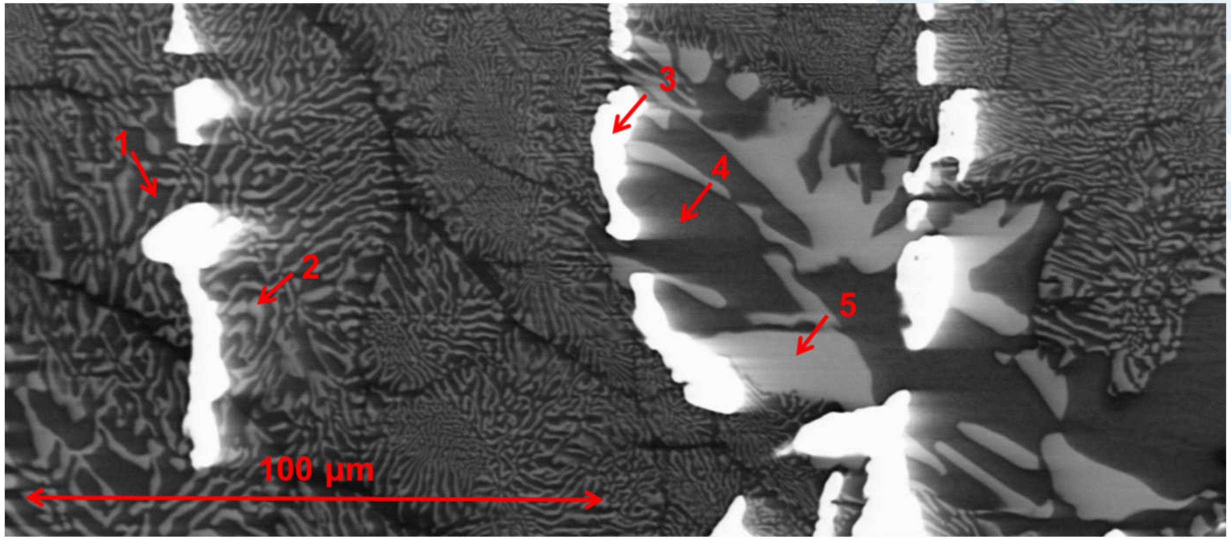
Note: Zr not associated with all high U concentration regions



Note: EDS results do not necessarily correspond to exact points in micrograph

	atomic %										
EDS Point	Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
1	0.4	0.0	2.3	0.0	78.6	5.5	0.0	0.0	0.0	0.0	13.2
2	8.4	1.7	76.0	1.1	0.0	0.5	0.0	2.0	3.5	0.4	6.4
3	1.3	0.4	50.2	1.7	0.0	0.0	4.0	11.4	3.2	0.0	27.9
4	1.1	0.0	3.6	0.9	0.0	0.0	0.0	0.0	67.8	0.0	26.7
5	13.1	2.0	75.1	0.3	0.0	4.7	0.6	0.4	0.0	1.0	2.9
6	0.6	0.0	2.8	0.0	88.6	5.7	0.0	0.0	0.0	0.0	2.4
7	6.1	1.0	36.9	1.2	0.6	0.6	0.0	0.0	37.5	0.0	16.1
8	10.6	1.5	57.0	0.7	0.0	10.2	1.6	2.3	0.7	0.0	15.4
9	2.6	0.4	46.8	2.8	0.0	0.0	3.5	12.2	7.2	0.0	24.5

HT9, Zr/U~1, Inert metals ~ 21w%



Note: EDS results do not necessarily correspond to exact points in micrograph

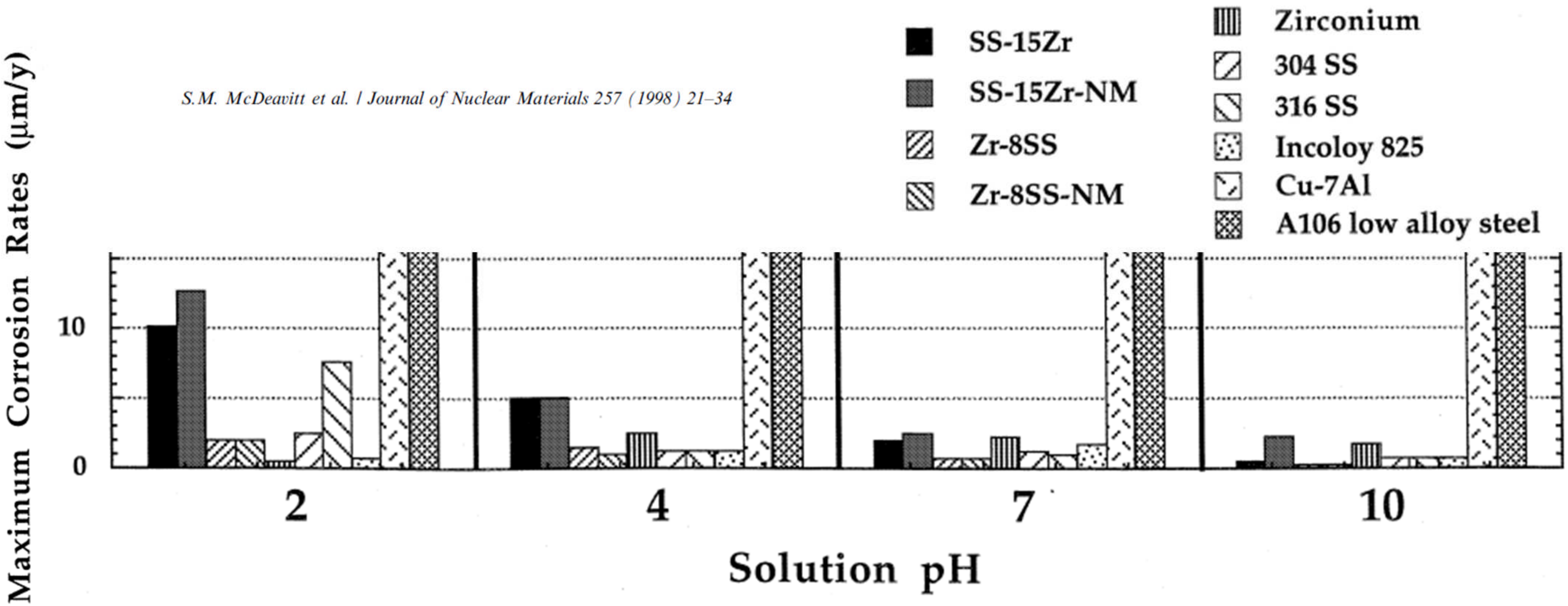
	atomic %										
EDS Point	Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
1	10.0	1.6	73.2	0.6	0.0	4.4	6.1	1.2	1.7	1.3	0.1
2	12.3	1.6	60.9	0.3	0.0	13.9	6.6	0.9	0.9	2.6	0.1
3	0.5	0.0	4.8	0.3	14.5	0.9	0.0	0.0	66.1	0.0	12.9
4	10.0	1.8	72.1	0.7	0.0	4.8	6.1	1.3	1.6	1.4	0.1
5	13.0	1.7	59.0	0.4	0.0	13.9	7.4	0.8	1.1	2.9	0.0

Conclusions for Variable Zr Content, 316SS vs. HT9 Cladding, and Increased Waste Loading

- **Possible 316 SS cladding effects with low Zr**
  - Two high Fe concentration phases, likely austenite and ferrite
    - *“ferrite” contains more Mo, Cr, and Re*
  - Additional high Pd concentration region found in low Zr alloys that also preferentially contains U, Rh, & Ni. But in a real waste form, there is unlikely to be a very high Pd concentration, unless there is a heavy waste loading.
  - At least 2, and likely 3 or more, Zr rich compositional ranges observed with differing U concentrations
  - Re (Tc surrogate) partitioning preference → ferrite > austenite >> $ZrFe_2$
  - Ni appears to be important in low Zr alloys for austenite formation and U segregation
- **Possible HT9 cladding effects with low Zr**
  - Zr not associated with highest U concentration regions at Zr/U~1/3, but Ni still is
  - Zr only (nearly) composition region observed throughout alloy
  - Lack of Ni important to morphological changes
- **Possible high waste loading with HT9 cladding and low Zr**
  - 3 primary phases (due to Mo?)
  - Microstructure appeared highly cracked

Future Work: Electrochemical Testing

- Previous research has indicated higher Zr contents roughly correlates to higher corrosion resistance
- Corrosion tests will occur in standard test solutions determined as part of multilab collaboration

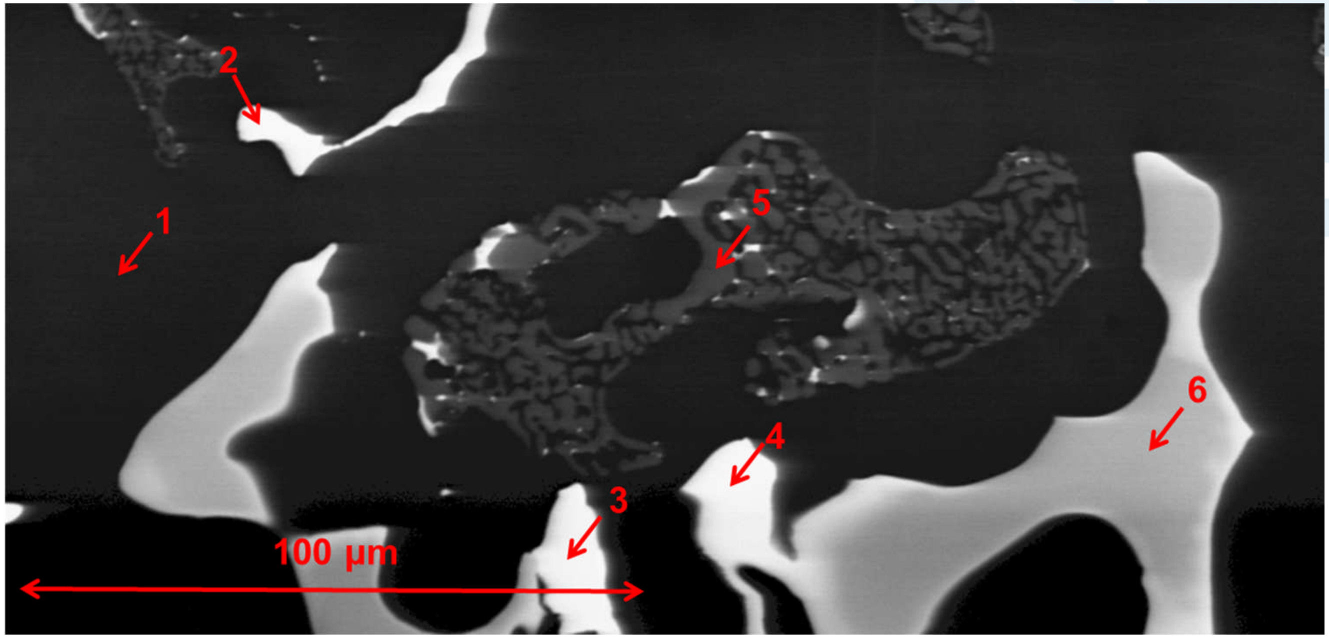


Thank You

Questions?

Extras

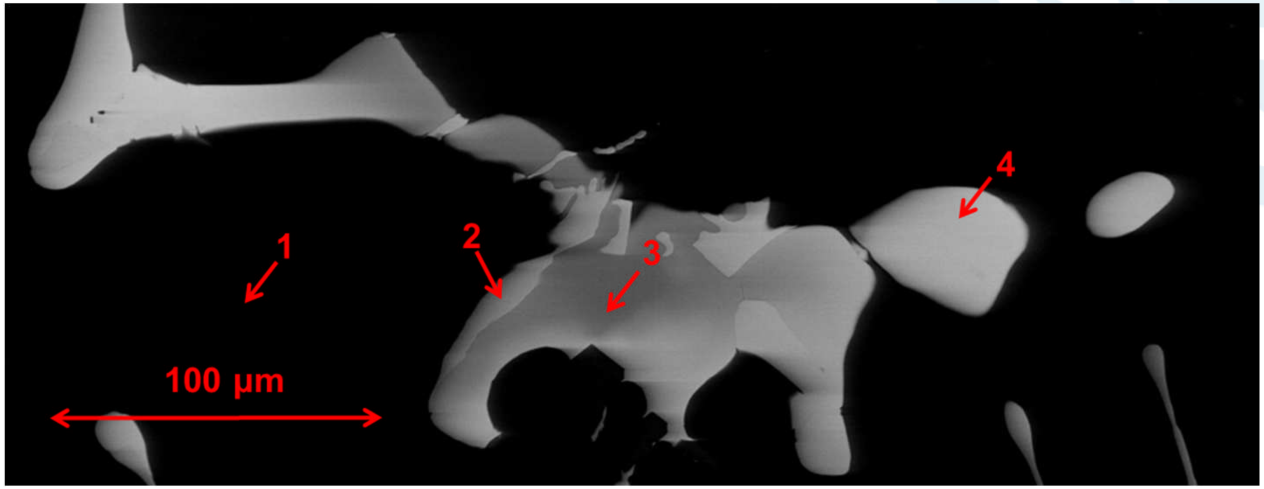
316SS, Zr/U~1



Note: EDS results do not necessarily correspond to exact points in micrograph

	atomic %										
EDS Point	**Cr**	**Mn**	**Fe**	**Ni**	**Zr**	**Mo**	**Ru**	**Rh**	**Pd**	**Re**	**U**
1	18.4	3.2	61.1	10.6	0.0	2.7	1.1	0.7	0.8	1.4	0.1
2	2.6	1.2	22.8	26.6	6.4	0.0	0.0	6.3	14.0	0.0	20.1
3	0.5	0.6	3.7	17.5	14.7	0.8	0.0	0.0	47.9	0.0	14.4
4	1.7	1.7	28.3	30.6	8.5	0.5	0.9	4.5	5.2	0.0	18.1
5	27.3	3.5	50.5	4.6	0.0	8.6	1.8	0.4	0.3	3.0	0.0
6	3.2	1.8	29.8	26.9	23.9	1.8	0.0	1.7	6.3	0.0	4.7

HT9, Zr/U~1



Note: EDS results do not necessarily correspond to exact points in micrograph

	atomic %										
EDS Point	Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
1	12.2	2.3	80.4	0.4	0.0	1.8	1.2	0.5	0.3	0.9	0.0
2	0.0	0.0	4.7	1.6	12.1	0.0	0.0	0.0	61.8	0.0	19.9
3	2.1	0.8	55.0	2.1	19.1	1.2	1.1	7.1	2.8	0.0	8.7
4	1.3	0.7	51.0	3.1	4.1	0.0	2.8	11.9	2.9	0.0	22.2

Impetus for Alloy Waste Form Compositional Study

- **Possible steps/options leading to higher waste loadings or different compositions:**
  - Anode basket is removed, and melted with UDS and cladding (likely) → More SS, lower waste loading
  - Oxide fuel used → oxide reduction and Li distillation steps likely required, decladding → much higher waste loading (on parr with RAW-1)
  - Metal fuel is declad, basket continuously refilled until ¾ full → much higher waste loading
  - Baskets are refilled, or dumped and refilled→ much higher waste loading

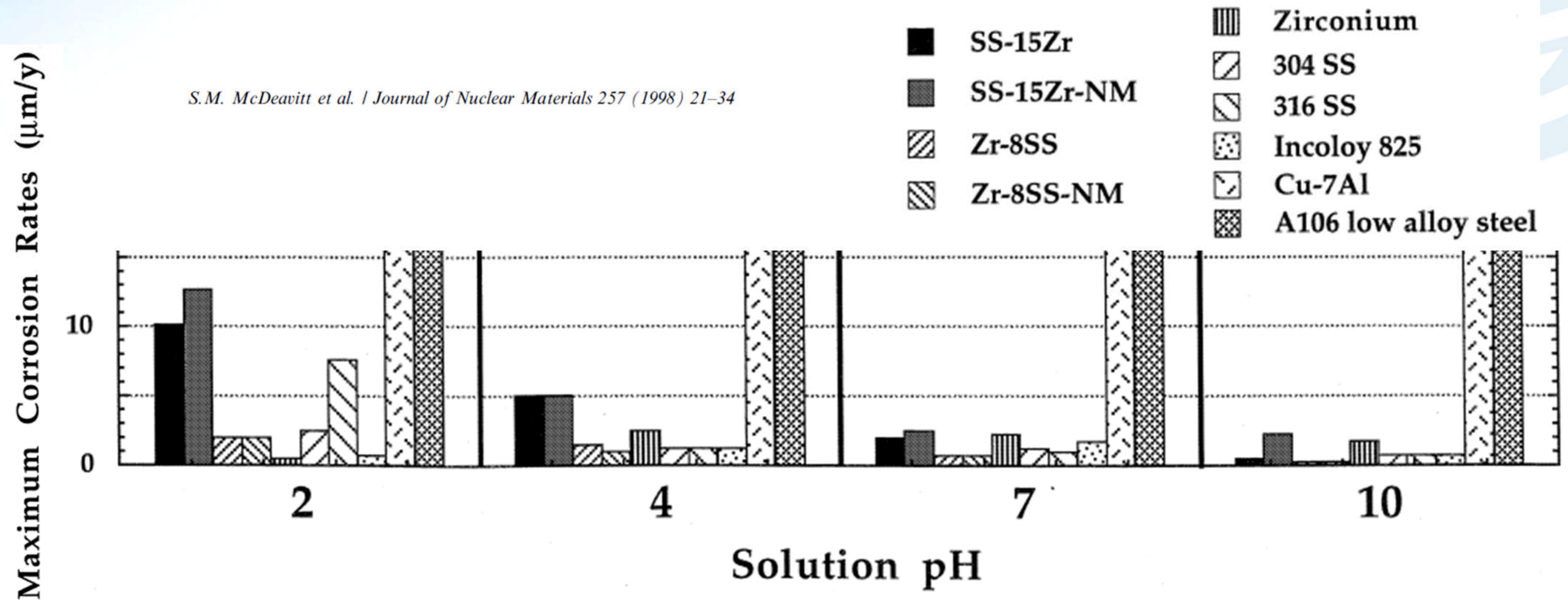
Electrometallurgical Processing Wastes

Alloy composition	Possible phase	Composition, at.% (±2 at.%)				
		Fe	Cr	Ni	Zr	U
SS–15Zr–5U	Ferrite	67.5	23.2	5	Neg.[a]	Neg.
	U-rich Laves	44.9	3.3	25.7	7.6	17.2
	Other Laves[b]	49.1	6	18	20.6	1.5
SS–15Zr–1Nb–1Pd–1Rh–1Ru–1Tc–2U	Ferrite	67.6	22.3	3.5	Neg.	Neg.
	U-rich Laves	43.2	3.3	22.5	10.9	12.2
	Other Laves	46.5	4.1	17.9	19.1	3
SS–15Zr–0.1Pd–0.6Ru–0.3Tc–11U	Ferrite	65.9	26.8	3.1	Neg.	Neg.
	U-rich Laves	49.3	3.1	18	8	19.3
	Other Laves	53.3	6.5	12.1	21.9	2.7
	$Fe_{23}Zr_6$-type	58.1	11	9.5	17.2	1.7

[a] Negligible.
[b] The designation 'Other Laves' represents areas in the Laves intermetallic away from the U-rich regions.

RAW-1(Re) SRNL										
	Cr	**Mn**	**Fe**	**Ni**	**Zr**	**Mo**	**Ru**	**Rh**	**Pd**	**Re**
ZrPd2	0.4	0.3	4.2	11.5	24.5	0	1.2	3.9	53.9	0
ZrFe2	4.7	1.1	36.6	13.5	24.7	3.6	8.5	1.8	5.4	0.2
Fe Solid Solution	15	1.7	65.3	8.7	0	4.3	3.9	0.1	0.6	0.4
MoFe2 (Dark)	21.2	1.5	52.6	4.4	0	13.3	5	0	0.4	1.6
MoFe2 (Light)	20.8	1	43.1	3.2	0	20.3	5.2	0	0.3	6.2

Alloy Composition Effects: Zr

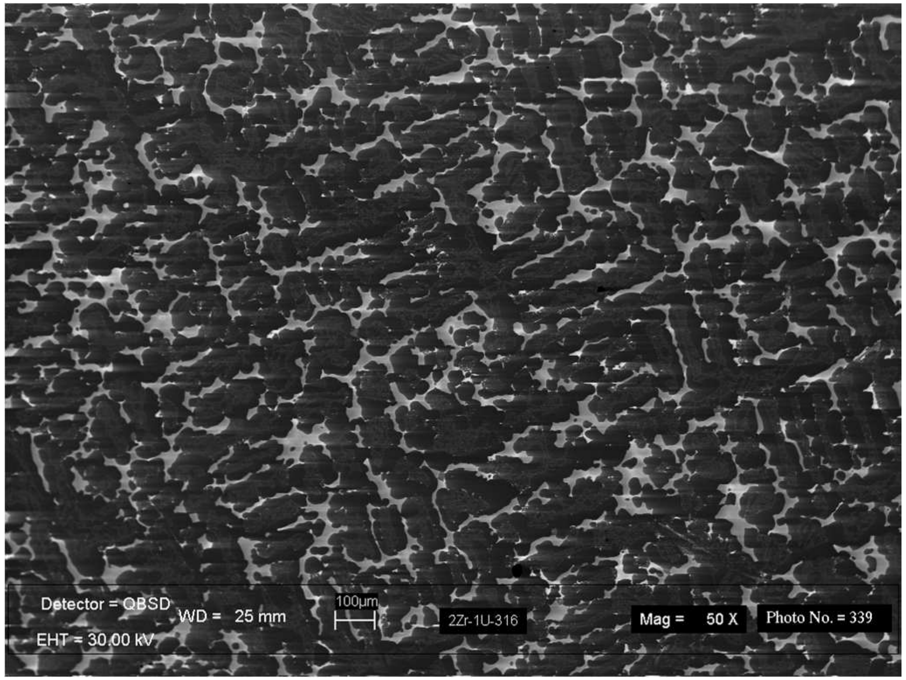


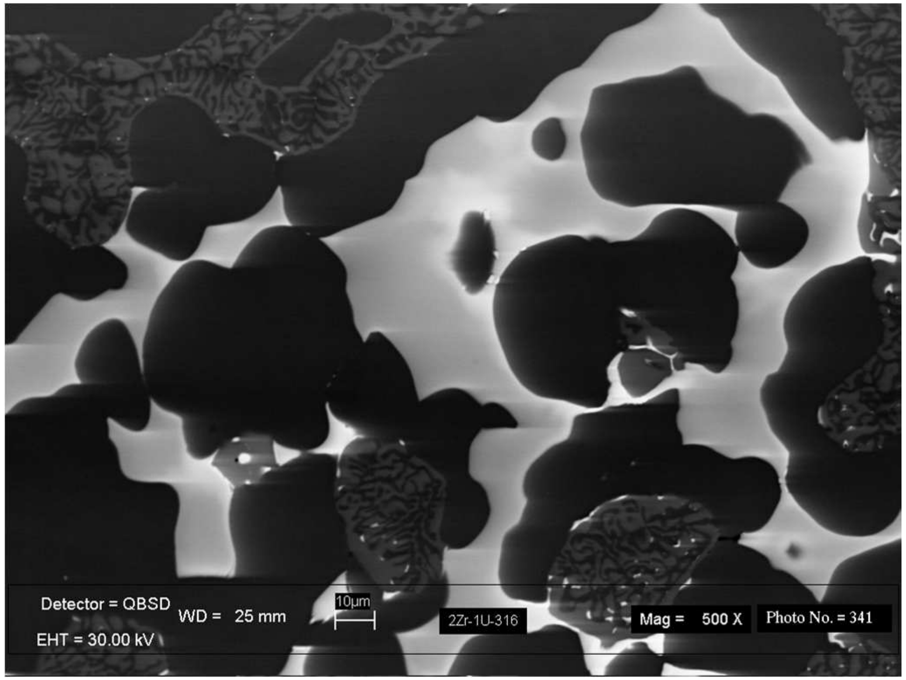
- **Based on EBR-II data, higher Zr content roughly leads to lower corrosion rates**

Zr Deficient Waste-Form , 316SS : Uranium Phase Reporting

- **Large area raster EDS: Zr/U~3.4**
- **From chemical loading : Zr/U~2**

Atomic %										
Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
18.2	3.6	58.8	11.3	2.2	2.9	0.8	0.5	0.8	0.4	0.7

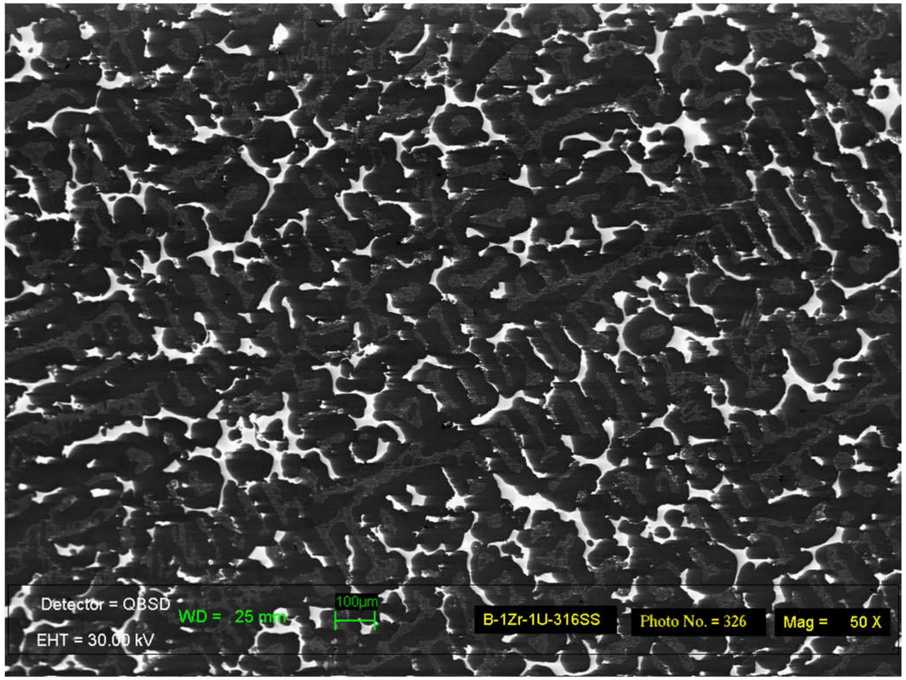


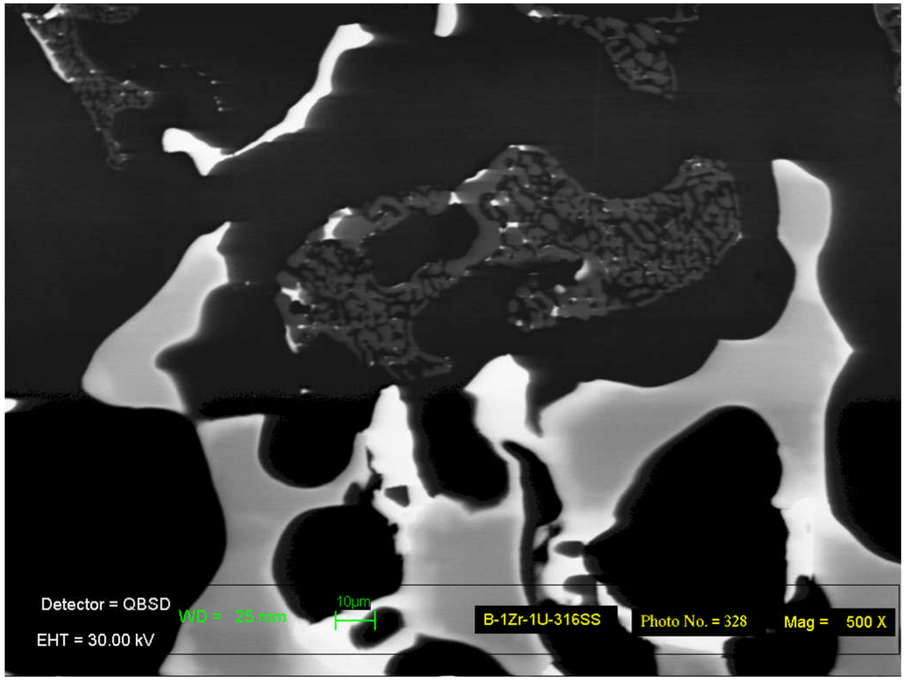


Zr Deficient Waste-Form , 316SS : Uranium Phase Reporting

- **Large area raster EDS: Zr/U~2.7**
- **From chemical loading : Zr/U~1**

Atomic %										
Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
18.8	3.1	58.2	10.6	1.6	3.2	1.0	0.7	1.1	1.1	0.6

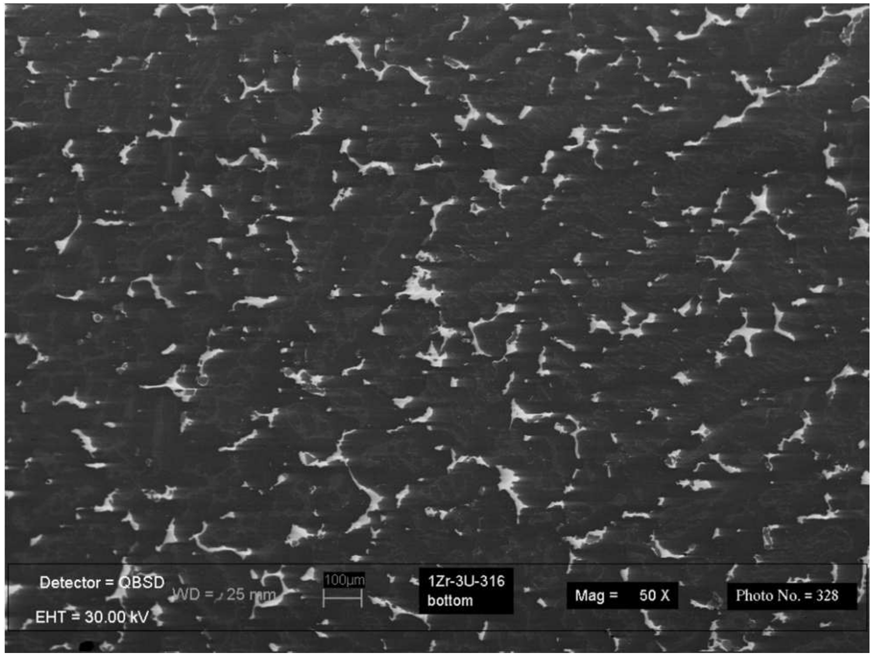


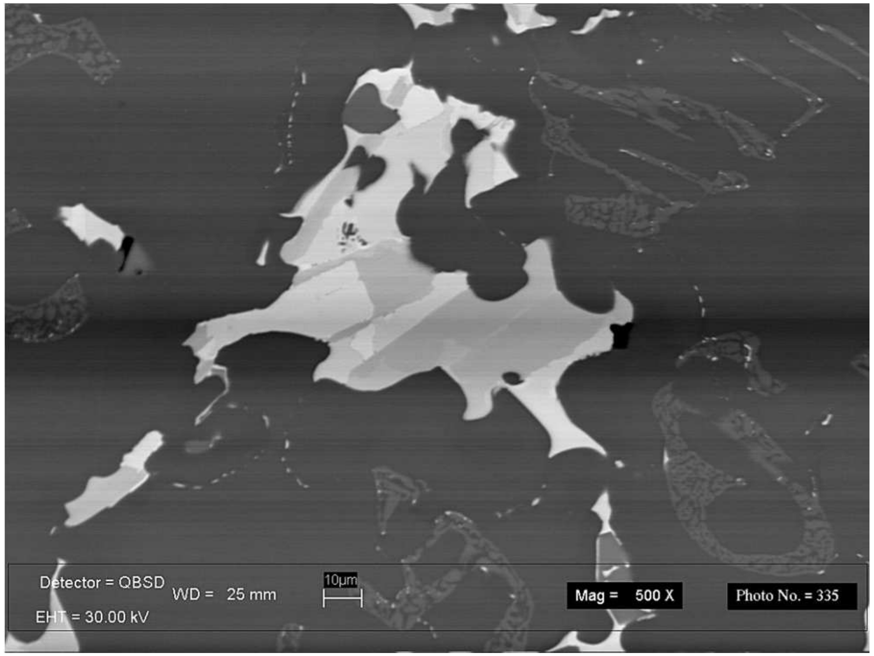


Zr Deficient Waste-Form, 316SS: Uranium Phase Reporting Zr/U~0.33

- **Large area raster EDS: Zr/U~1.1**
- **From chemical loading: Zr/U~0.33**

Atomic %										
Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
18.8	3.3	58.6	10.6	0.7	3.3	1.1	0.6	1.1	1.3	0.6

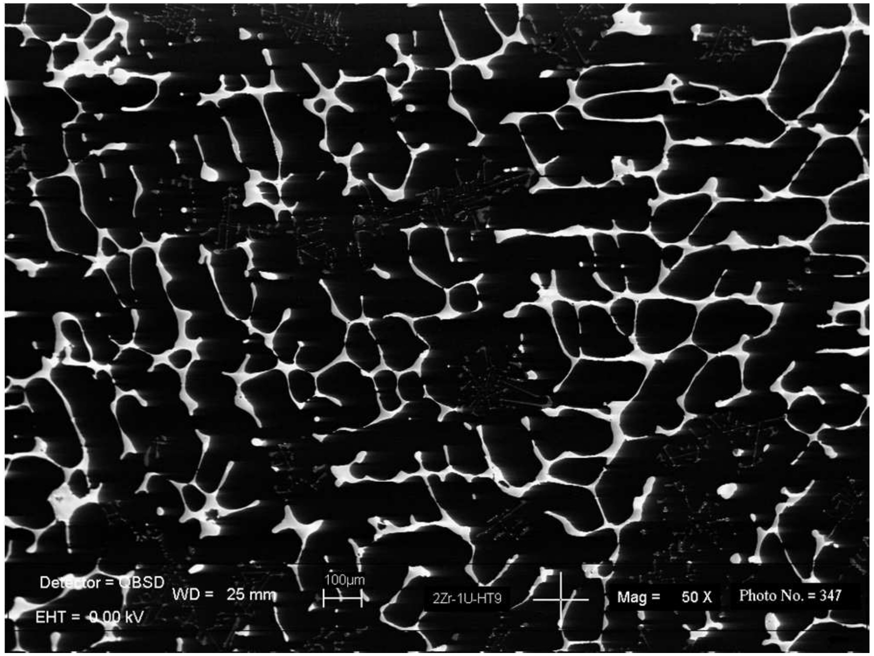


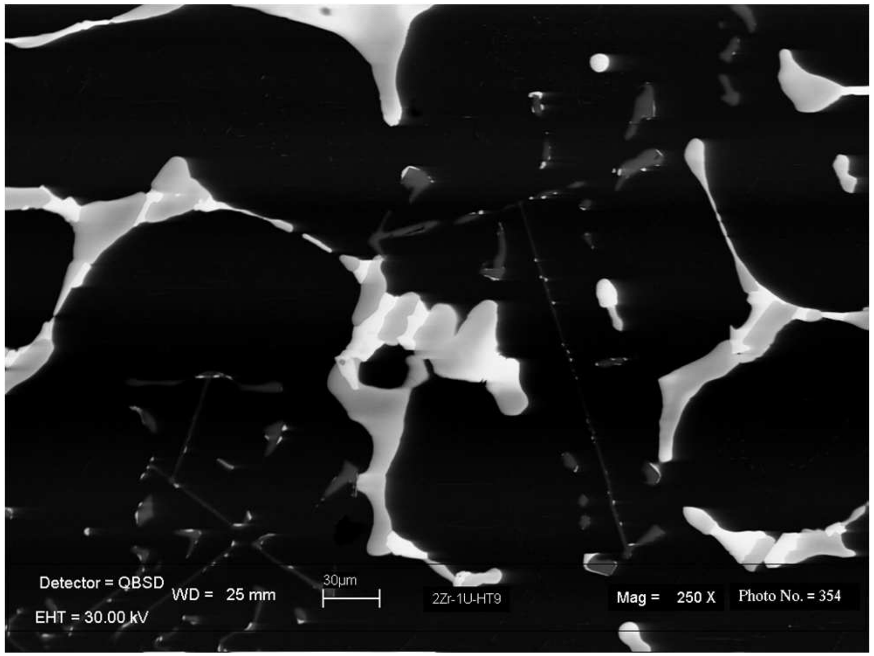


Zr Deficient Waste-Form, HT9: Uranium Phase Reporting

- Large area raster EDS: Zr/U~4.2-7.3
- From chemical loading : Zr/U~2

Atomic %										
Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
12.0	2.3	78.8	0.5	2.8	1.8	0.6	0.2	0.5	0.0	0.7

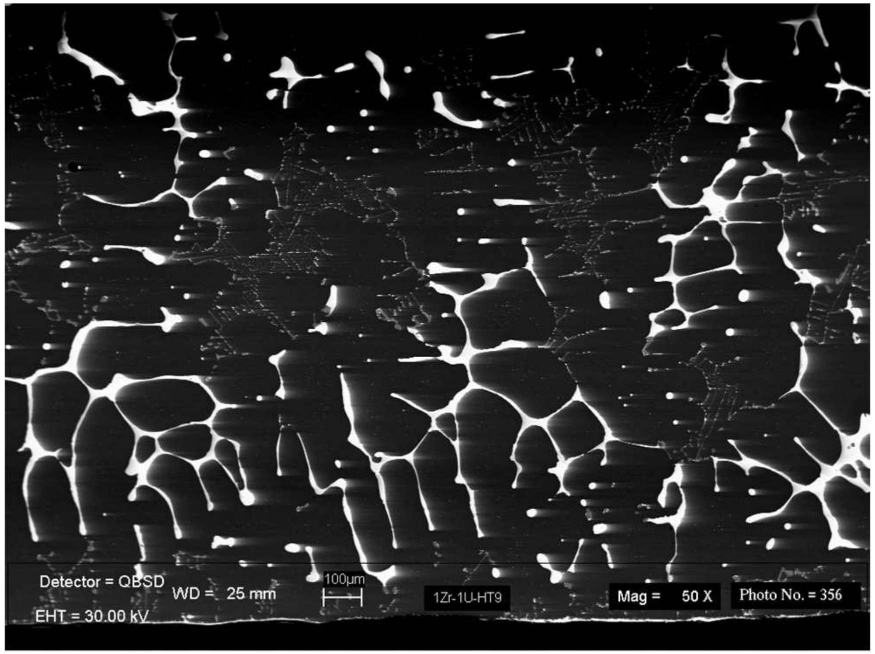


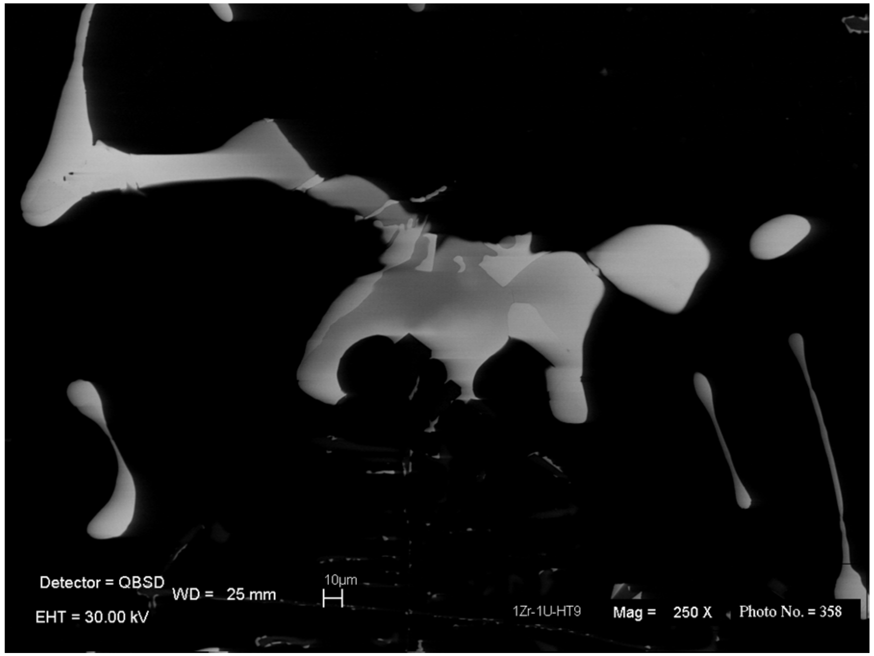


Zr Deficient Waste-Form, HT9: Uranium Phase Reporting

- **Large area raster EDS: Zr/U~3.6-4.5**
- **From chemical loading : Zr/U~1**

Atomic %										
Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
12.1	2.4	79.2	0.5	1.6	1.9	0.6	0.3	0.6	0.5	0.4

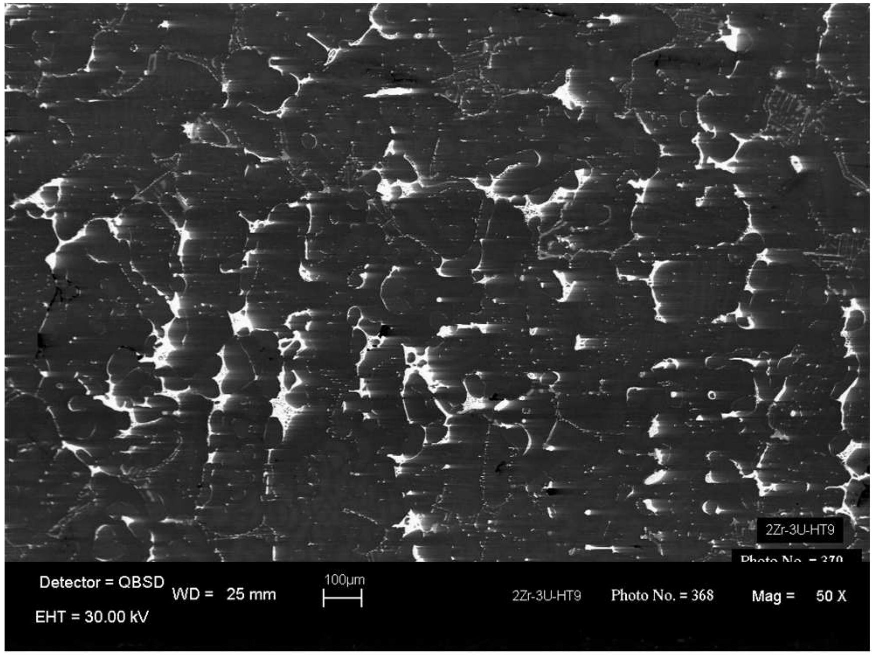


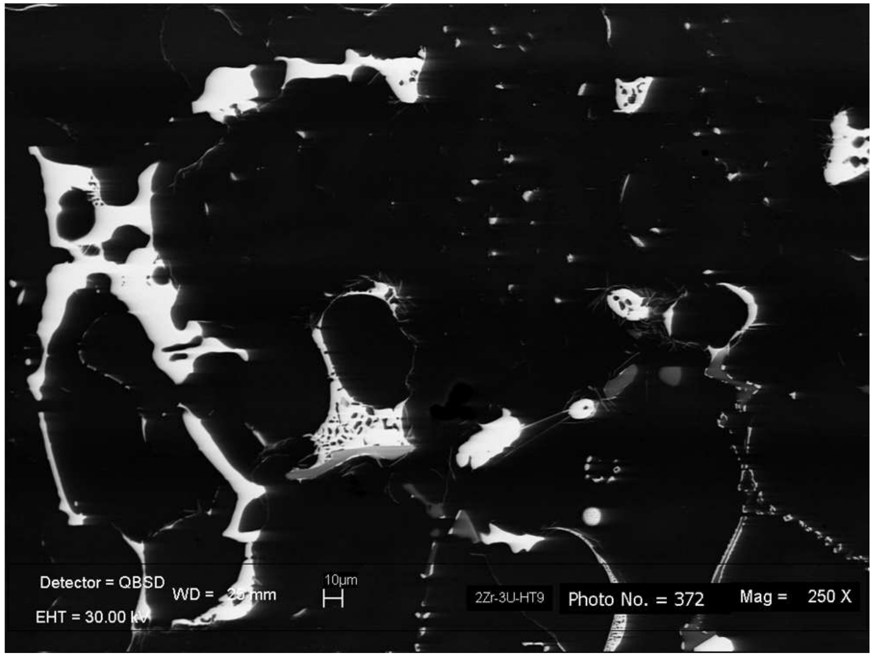


Zr Deficient Waste-Form, HT9: Uranium Phase Reporting

- **Large area raster EDS: Zr/U~2.3-3.9**
- **From chemical loading : Zr/U~1/3**

Atomic %										
Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
12.4	2.1	78.8	0.5	1.1	2.1	0.8	0.5	0.7	0.7	0.5





Higher Waste Loading Effects in a Zr Deficient Waste-Form with HT9: Uranium Phase Reporting

- Large area raster EDS: Zr/U~1.7
- From chemical loading : Zr/U~1

Atomic %										
Cr	Mn	Fe	Ni	Zr	Mo	Ru	Rh	Pd	Re	U
10.8	1.6	68.1	0.4	1.0	7.5	5.0	0.0	3.6	1.4	0.6